28436

IGM88TC-307-661-G
CNRC 28436

PRODUCTION OF SiC IN A THERMAL PLASMA

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ABSTRACT

The needs of high temperature structural ceramics have rekindled great interest in developing methods for producing high-purity, ultrafine powders. Among different ways of fine powder preparation, gas phase synthesis in a thermal plasma is one of the most important techniques. A continuous thermal plasma process has been developed to produce ultrafine SiC powders by gas phase synthesis from silicon tetrachloride and methane in an argon and argon + hydrogen plasma jet. The reaction conditions to control the physical and chemical properties of the powders have been investigated.

Bulk properties of SiC powders were determined by X-ray diffraction and Fourier transform infrared spectroscopy. Surface characteristics and particle size were examined by scanning electron microscopy.

It is found that the reaction conditions have significant effects on the size and composition of particles. The particles, 0.1-0.5 μm in size, can be either completely amorphous or crystalline β-SiC. The presence of Si-O bonds is detected in all powders and the amount of oxygen strongly depends on the operating conditions used.

Gas phase synthesis in a thermal plasma can be an efficient means for producing, on a continuous basis, ultrafine particles of different compositions and morphologies.

KEYWORDS

Ultrafine powder; β-SiC particle; thermal plasma; FTIR; gas phase synthesis.

INTRODUCTION

Recently, there have been increasing needs for ultrafine refractory powders as a new technology advances. Among many new powder preparation techniques, the plasma technique is receiving considerable attention for the production of ultrafine particles of metals and nonmetallic materials.

Ultrafine powders, because of lower temperature and pressure sinterability, have an advantage over conventional standard powders for producing solid materials.

Silicon carbide has been a leading candidate as a high temperature engineering material for gas turbines and heat engines. This is because its strength, hardness and resistance to both thermal shock and oxidation (up to 1473 K) make it an ideal choice in harsh working environments.

At the present time, silicon carbide powders are most commonly prepared by four methods, namely: carbothermic reduction of silica (or Acheson process), gas phase process, sol-gel process and polymer pyrolysis.

The powder process properties such as impurity level and uniformity of particle size etc. strongly depend on the preparation routes. Among these methods, the gas phase process appears to be the most promising, because it not only gives improved control over particle size and morphology as well as purity, but also has potential for large-scale production on a continuous basis[1].

It has been reported[2-7] that silicon carbide can be produced with dc or rf thermal plasmas. Both silicon powder, silicon tetrachloride or silane were used as a reactant. We have attempted to produce ultrafine SiC powders of different sizes and compositions under various operating conditions. The main objectives of this work were to identify the major variables affecting the properties of the powders produced in a dc thermal plasma and to evaluate the technical feasibility of producing them continuously. Some of the preliminary results will be reported in this paper.

EXPERIMENTAL

The test apparatus is shown schematically in Figure 1. It consists of a d.c. power supply (75 kW) and a control console, a reactor system, reactants feeding system, gas supply system, water-cooling system and an exhaust cleaning system. The reactor system consists of three major components: a d-c torch, a water-cooled mixing head containing a graphite sleeve and a water-cooled collecting chamber. After the d.c. torch is ignited under inert atmosphere and the proper gas plasma is established, the liquid $SiCl_4$ (b.p.=57.6C°) is transferred from the reservoir to the flash boiler by a peristaltic pump. The vaporized $SiCl_4$ generated from the flash boiler is then injected to the plasma jet with or without a carrier gas through a single (or multi-orifice) orifice. To make the vaporization of the liquid $SiCl_4$ instantaneous, the flash boiler temperature is maintained between 100 and 400°C depending on the flow rates. The vapor transfer line is also heated to prevent any condensation of the vapor. The carbon bearing gas (or CH_4) is injected either just below the $SiCl_4$ injection point through 4-radial holes or further downstream via a circumferentically radial slit in a quenching ring. Argon and/or hydrogen were used as carrier gases. A thermocouple was situated at the exit of the quenching ring to measure an average gas temperature. Fine product powders are deposited on the inner walls of the chamber and a separator at the bottom. The hot gaseous chamber effluent containing finer powders passes through cyclones, condensers, porous metallic filters and caustic absorbers to remove the products and acidic by-products.

The prepared powders were analyzed by various methods including X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), BET analysis and wet chemical analysis. For FT-IR analysis, the powders were mixed with potassium bromide at a concentration of 0.5-1.5% by weight and the spectra were recorded by diffuse reflection using neat potassium bromide as a reference.

RESULTS AND DISCUSSION

Four sets of experiments were conducted to determine the physical and chemical properties of the products powders under various operating conditions and their results are summarized in Table I.

Runs 1 and 2 were conducted to determine the effects of methane concentration on the nature of the silicon carbide produced. A mixture of methane and hydrogen was injected below a mixing sleeve through a circumferentially radial slit in a quenching ring (25.4 mm ID) in an argon + hydrogen plasma. The mixing sleeve had 25.4 mm ID and was 50.8 mm long. The methane flow rates used were 1.7 (70% more than stoichiometric) and 3.4 l/min., respectively. Powder samples for analyses were collected in open air from the metallic filter element by scraping the deposited cakes. No special handling procedures were applied to prevent oxygen contamination. The produced powders were grey but darker with increased CH_4 flow rate. XRD analysis showed that the two samples had similar peak patterns and consisted of well-defined crystalline β-SiC. Figure 2 shows a typical XRD diagram of the samples. SEM analysis showed no significant difference between the samples in shape and size. As expected from a gas phase reaction, the majority of particles were round and ~ 0.1μm in size (Figure 3). BET analysis gave a specific surface area of ~ 92 m^2/g.

The FT-IR spectra, shown in Figure 4, reveal a very strong Si-C bond at 950-800 cm^{-1} and weak Si-O absorption at 1200-1000 cm^{-1}. The somewhat higher "baseline" level in Run 2 may be due to a higher content of free carbon as a result of the higher CH_4 flow rate. The oxygen may have originated from: i) oxygen present in the plasma gases and reactants (CH_4 and $SiCl_4$); ii) direct oxidation between samples and oxygen; iii) the reaction between chlorides and air. However, the major source of oxygen is not identified at this moment.

Runs 3 and 4 were intended to determine the effect of quenching on the prepared powders in a pure argon plasma. Hydrogen was used to control the quenching rate. In run 3, the produced powder was grey in color and showed well-defined crystalline β-SiC (XRD) with a weak Si-O bond (FTIR), although the reaction temperature dropped by 300 K compared to run 1. When the reaction temperature dropped further to ~ 1000K as the quenching hydrogen flow increased (run 4), the produced power exhibited a mixture of amorphous and crystalline β-SiC phases.

Runs 5 and 6 were essentially repetitions of runs 3 and 4 using a larger diameter mixing sleeve (38.1 mm ID). The tests were aimed to see the effects of the reaction temperature as well as the sleeve geometry on the properties of the powders produced. It is expected that the gas temperature in the reaction region using the larger sleeve is lower than that obtained with the smaller one at a given arc power. In test 5, the reaction temperature was decreased from 1190K (run 3) to 1069K. A brown powder was collected and analyzed by XRD and SEM, which showed the characteristics of a mixed amorphous and crystalline β-phases. The particles were mainly round and about 0.1 μm in size. FTIR showed the presence of relatively strong Si-O and OH bonds.

In test 6, higher quenching gas was used to produce a completely amorphous product. The corresponding reaction temperature was 140K lower than that in run 5. The prepared powder was light brown in color. Analyses by XRD and SEM clearly indicated that the powders were mainly amorphous with traces of crystalline phases. Typical particles were round and about 0.2 μm in size. Compared to more crystalline powders (for example, run 1), the amorphous powders looked more fluffy and consisted of agglomerates with several individual particles, which may

be attributed to the fact that amorphous fine powders are easily oxidized and decomposed in air. FTIR analysis showed the presence of a very strong Si-O absorption, much stronger than the Si-C band and confirmed the vulnerability to oxidation of amorphous fine powders. A preliminary wet chemical analysis showed that the amorphous powders contained a large amount of oxygen and chlorine. Although further work is required to identify the source of oxygen contamination, it may be said, on the basis of the data collected from the last four runs, that powders with different morphologies and sizes can be produced by controlling the quenching rate (or reaction temperature). It also appears that the reaction temperature should be at least 1150K to produce crystalline β-SiC and below 1000K for amorphous SiC.

Finally, runs 7 through 9 were conducted to determine the effect of the position of methane entrance on the nature of the silicon carbide produced. A mixture of CH_4 and H_2 was introduced just below the silicon tetrachloride injection point into the mixing sleeve (38.1mm ID). There was a steep radial temperature gradient in the sleeve ranging from 500 near the wall to above 1623K near the center line (run 7). The average temperature in the reaction region was estimated to be approximately 2000K. The produced powders were typically grey but darker with increased CH_4 flow rate. Analyses by XRD and SEM indicated that the powders were crystalline β-SiC and very similar to those obtained from runs 1 and 2. However, the FTIR spectra showed a somewhat stronger Si-O absorption at 1200-1000 cm^{-1} and an OH band at 3700-3000 cm^{-1}. The higher oxygen contamination in these samples in spite of higher reaction temperature may be due to the fact that incomplete mixing among the reactants and a temperature gradient in the reaction zone cause the formation of unreacted or partially converted subchlorides which readily react with air to form oxides. Consequently, the effect of CH_4 concentration on the degree of carbon content in the products could not be established. Nevertheless, this test clearly demonstrated the importance of reactant mixing and temperature to control the properties of the final products.

CONCLUSIONS

1) A continuous thermal plasma process has been developed to produce ultrafine SiC powders with different chemical and physical properties by gas phase synthesis from silicon tetrachloride and methane in an argon and argon + hydrogen plasma jet.

2) In order to produce ultrapure powders, a special handling technique is required to remove oxygen and oxygen-sensitive impurities. Especially, complete elimination of volatile chlorides is essential.

3) The reaction conditions have significant effects on the properties of the powders produced. It is found that:

   a) the reaction temperature and the quenching rate are the most critical factors to determine the morphologies and sizes of the products.

   b) the levels of impurities in the product strongly depend on the degree of the reactant mixing.

   c) crystalline β-SiC powders are formed at reaction temperature above 1150K and amorphous SiC powders below 1000K.

   d) the particles are round in shape and 0.1-0.5μm in size.

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TABLE 1 - SUMMARY OF EXPERIMENTAL CONDITIONS

Run	Arc Power	Plasma gas		Reactant 1		Reactant 2		Quenching gas			Gas Temperature	
		Ar	H_2	$SiCl_4$	Carrier (Ar)	CH_4	Carrier (H_2)	CH_4	Ar	H_2	T_w[1]	T_o[2]
	kW	1/m	1/m	gm	1/m	1/m	1/m	1/m	1/m	1/m	°C	°C
1	10.5	24	2	7.5	2	-	-	1.7	-	44	1049	1215
2	11.2	24	2	7.5	2	-	-	3.4	-	44	1038	1204
3	7.2	24	-	7.5	2	-	-	3.4	-	35	699	917
4	7.2	24	-	7.5	2	-	-	3.4	-	70.4	617	836
5	7.5	24	-	7.5	2	-	-	3.4	-	35	575	796
6	7.5	24	-	7.5	2	-	-	3.4	-	70.4	464	654
7	7.5	24	-	7.5	2	1.7	53	-	8	-	542	763
8	7.5	24	-	7.5	2	3.4	53	-	8	-	532	754
9	7.2	24	-	7.5	2	6.8	53	-	8	-	516	738

1. Gas temperature near the wall at the exit of the quenching ring
2. Gas temperature near the center at the exit of the quenching ring

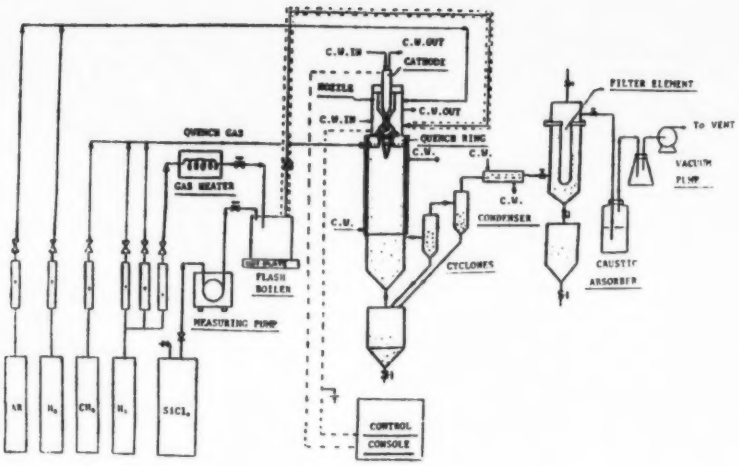

Fig. 1 - Schematic diagram of experimental apparatus

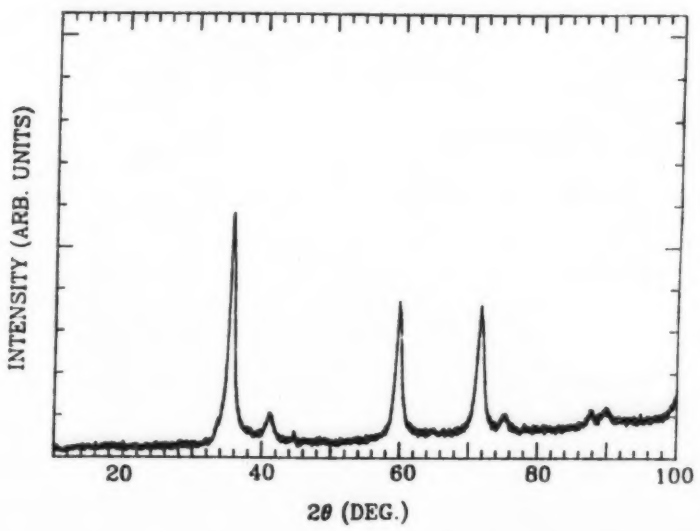

Fig. 2 - Typical X-ray diffraction patterns of the prepared β-SiC

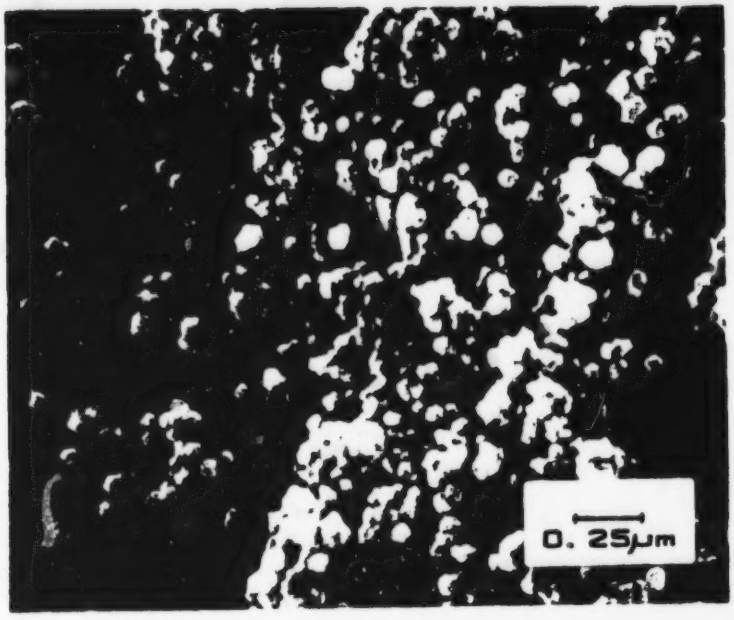

Fig. 3 - Typical scanning electron micrograph of β-SiC particles

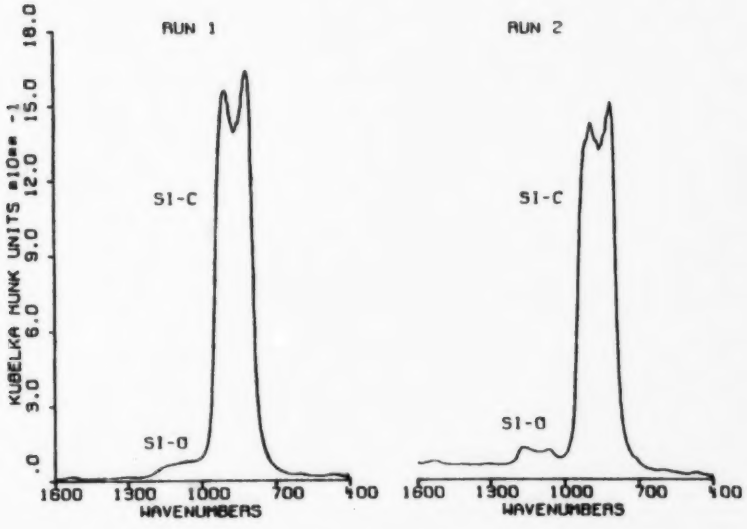

Fig. 4 - Typical Fourier Transform IR spectra of β-SiC